

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/803,126
Inventor(s) : James Robert Schwartz et al.
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Title : AUGMENTATION OF PYRITHIONE ACTIVITY OR A
POLYVALENT METAL SALT OF PYRITHIONE ACTIVITY BY
ZINC-CONTAINING LAYERED MATERIAL

DECLARATION OF JAMES R. SCHWARTZ UNDER 37 CFR 1.132

Commissioner for Patents
PO Box 1450
Alexandria, VA 22312-1450

Dear Sirs:

I, James Robert Schwartz, hereby declare and say the following:

1. I have been a full-time employee of The Procter & Gamble Company for 23 years and my current position with the company is Research Fellow, P&G Beauty. I hold a B.A. in Chemistry from Kenyon College, 1982 and a PhD in Chemistry from the University of Illinois, 1986.
2. I am one of the named inventors on the above-entitled application and am familiar with the November 25, 2009 Office Action in this application.
3. The claimed invention in the above-entitled application:

A composition comprising:

- a) from about 0.01 weight% to about 5 weight%, based on the total weight of the composition, of pyrithione or a polyvalent metal salt of a pyrithione, wherein the pyrithione or polyvalent metal salt of pyrithione is zinc pyrithione;

b) from about 0.001 weight% to about 10 weight%, based on the total weight of the composition, of a zinc-containing layered material which provides an augmentation factor greater than 1 wherein the zinc-containing layered material comprises an impurity containing hydroxy-containing basic zinc carbonate and further wherein the ratio of zinc-containing layered material to said pyrrhione or a polyvalent metal salt of pyrrhione is from about 1:2 to about 3:1.

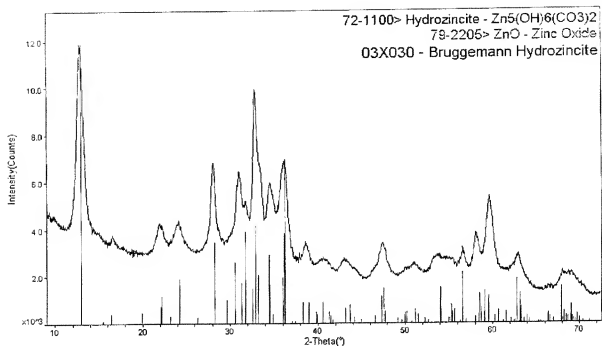
4. Bhat et al. in WO 96/25913 describes the preparation and use of a material termed "monophasic zinc hydroxycarbonate." As described by Bhat et al., hydrozincite (naturally occurring) and basic zinc carbonate are equivalent names for zinc hydroxycarbonate (Page 1, lines 23-24 and line 35). The term "monophasic" is defined (Page 1, lines 29-33) as "without any other impurity phases ... present ..."

Within the field of x-ray diffraction of crystal structures, "monophasic" means that only a single material is identifiable by its x-ray diffraction pattern. For example, a representative article in the field describes the synthesis of a monophasic solid $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ verified by observing only the peaks in the diffraction pattern associated with this material ((J Mater Sci (2207) 42:3557-3563); Page 3560; attached). When different preparative conditions are used, multiple phases are observed to be present in the diffraction spectra (Page 3561).

5. X-ray diffraction is generated for various sources of basic zinc carbonate materials. X-ray diffraction is generated for various sources of basic zinc carbonate materials. The data were collected on a Stoe STADI-P transmission mode diffractometer. The generator was operated at 40kV/50mA, powering a copper anode long-fine-focus Cu x-ray tube. The diffractometer incorporates an incident-beam curved germanium-crystal monochromator, standard incident-beam slit system, and a curved position-sensitive detector with an angular range of about 37.5° 2θ . Data were collected in transmission mode over a range of 7 to 44° 2θ .

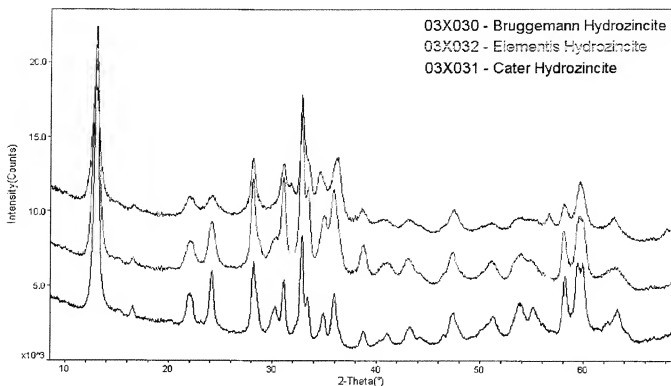
The most effective basic zinc carbonate materials of the claimed invention (e.g., from Bruggemann) are composed of more than one phase (i.e., is not monophasic) as evidenced by additional peaks (highlighted in yellow) beyond those that represent pure basic zinc carbonate, demonstrated below as Hydrozincite.

TABLE 1



6. When using x-ray diffraction to compare different commercial sources of basic zinc carbonate, i.e. Bruggemann, Elementis, and Cater, some appear primarily monophasic while others do not:

TABLE 2



While the sample in Table 2 from Bruggemann is multi-phasic as evidenced by additional peaks highlighted in yellow, the samples from Cater and Elementis show less evidence of this (noting also the broader peaks in the Bruggemann spectrum – another indication of multi-phasic nature).

7. Further, these difference of monophasic vs. multi-phasic are important to the behavior of basic zinc carbonate, as the higher purity materials (closer to monophasic) have lower relative zinc lability, as demonstrated in Table 3.

Zinc lability is a measure of the chemical availability of zinc ion. Soluble zinc salts that do not complex with other species in solution have a relative zinc lability, by definition, of 100%. The use of partially soluble forms of zinc salts and/or incorporation in a matrix with potential complexants generally lowers the zinc lability substantially below the defined 100% maximum.

Zinc lability is assessed by combining a diluted zinc-containing solution or dispersion with the metallochromic dye xylenol orange (XO) and measurement of the degree of color change under specified conditions. The magnitude of color formation is proportional to the level of labile zinc. The procedure

developed has been optimized for aqueous surfactant formulations but may be adapted to other physical product forms as well.

A spectrophotometer is used to quantify the color change at 572 nm, the wavelength of optimum color change for XO. The spectrophotometer is set to zero absorbance at 572nm utilizing a product control as close in composition to the test product except excluding the potentially labile form of zinc. The control and test products are then treated identically as follows. A 50µl product sample is dispensed into a jar and 95 ml of deaerated, distilled water are added and stirred. 5mL of a 23mg/mL xylenol orange stock solution at pH 5.0 is pipetted into the sample jar; this is considered time 0. The pH is then adjusted to 5.50 ± 0.01 using dilute HCl or NaOH. After 10.0 minutes, a portion of the sample is filtered (0.45µ) and the absorbance measured at 572nm. The measured absorbance is then compared to a separately measured control to determine the relative zinc lability (zero TO 100%). The 100% lability control is prepared in a matrix similar to the test products but utilizing a soluble zinc material (such as zinc sulfate) incorporated at an equivalent level on a zinc basis. The absorbance of the 100% lability control is measured as above for the test materials.

CRYSTALLINITY METHODOLOGY

The FWHM (full-width-half-maximum) of each reflection in an x-ray diffraction (XRD) pattern is a measure of crystalline imperfections and is a convolution of instrumental and physical factors. True sample broadening can be deconvoluted from instrumental broadening via the following expression.

$$\text{FWHM (S)}^D = \text{FWHM (I+S)}^D - \text{FWHM (I)}^D$$

Where FWHM (S) is the true specimen broadening, FWHM (I+S) is the combined broadening, FWHM (I) is the instrument broadening parameter and D is the deconvolution parameter. For this analysis the parameter D was set to 2.

The appropriate standard reference material (SRM), known to have no inherent sample broadening effects, and has reflections close, in 2-theta, to the sample reflection of interest should be used to obtain the instrument-broadening function.

In general, the choice of SRM to use for the instrument correction for a particular specimen is based on the 2θ value of the specimen reflection of interest. As a matter of principle, the range of the SRM's reflections should overlap the 2θ value of the particular reflection of the specimen. For example if one is interested in the (101) reflection of ZnO which occurs around 36-degrees 2θ, silicon SRM which covers about 28 to 88 degrees 2θ might be an appropriate choice. Similarly, for (104) reflection of smithsonite mineral occurring at about 32-degrees 2θ, silicon SRM can be used for the instrument correction. For bigger structures with lower 2θ values, silver behenate with a basal reflection at about 4-degree 2θ would be recommended.

And so it was that in the case of the (200) reflection of zinc carbonate whose 2θ value occurs at about 13-degrees, National Institute of Standards and Technology (NIST) SRM #675 (mica) was used. The range of reflections for mica is about 8 to 85 degrees in 2θ using a normal sealed tube with Cu radiation.

Crystallite Size of Particulate Zinc Materials

Once the true specimen FWHM has been obtained as described above, crystallite size (XS) may be derived from the Scherrer equation:

$$XS = K * \lambda / (FWHM (S) * \cos (\theta))$$

Where K is the shape factor of the average crystallite, set at 0.9, the FWHM (S) value is in radians, $\cos (\theta)$ is the position of the specific, single, well-resolved peak that is most sensitive to the desired physical property of the material.

Crystallite Size for Basic Zinc Carbonate

Following the prescribed approach above, crystalline imperfection has been assigned to various basic zinc carbonate samples.

Three peaks (200, $\sim 13^\circ 2\theta$, 6.9Å; 111, $\sim 22^\circ 2\theta$, 4.0Å; 510, $36^\circ 2\theta$, 2.5Å) are found to be sensitive to crystalline imperfections; the (200) reflection are selected for the analysis, as it is the most sensitive and well-resolved. Peaks are individually profile-fitted using normal Pearson VII and Pseudo-Voigt algorithms in Jade 6.1 software by MDI. Each peak is profile fitted 10 times with changes in background definition and algorithm to obtain average FWHM with standard deviations. The value of the instrument-broadening parameter derived from the FWHM vs. 2θ curve at the location of the (200) reflection of hydrozincite is 0.373. Listed in the Table 3 below are the FWHM values and the derived crystallite sizes using the (200) peak.

TABLE 3


Sample	(200) Peak		FWHM (S)	Crystallite Size (XS, Å)	Relative Zinc Lability (%)
	FWHM (I+S)	Std. Dev.			
Brüggemann Zinc Carbonate	0.8625	0.0056	0.778	103	56.9
Cater Zinc Carbonate	0.4982	0.0023	0.330	243	42.3
Elementis Zinc Carbonate	0.7054	0.0024	0.599	134	51.6

The larger the FWHM, the smaller the crystallite size, the greater the crystalline imperfection and the lower the crystallinity. Thus, the crystallinity is in the order: Brüggemann < Elementis < Cater. The zinc lability increase as the crystallinity decreases, suggesting lower crystallinity (or smaller crystallite size) is more preferable to maximize zinc lability.

Such difference of monophasic vs. multi-phasic are important to the behavior of basic zinc carbonate, as the higher purity materials (closer to monophasic) have lower relative zinc lability, as demonstrated in Table 3.

In summary, this data demonstrates that Brüggemann-type basic zinc carbonate materials are not monophasic and that this is an important attribute of the claimed invention to achieve high performance.

8. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, Title 18, of the United States Code, and that such willful false statements may jeopardize the validity of the above-identified application of any patent issued thereon.


 James Robert Schwartz
 Dated: 25 May 2016

18 U.S.C §1001 Statements or Entries Generally

Whoever, in any matter within the jurisdiction of any department or agency of the United States knowingly and willfully falsifies, conceals, or covers up by any trick, scheme, or device a material fact, or makes any false, fictitious or fraudulent statements or representations, or makes or uses any false writing or document knowing the same to contain any false, fictitious, or fraudulent statement or entry shall be fined no more than \$10,000 or imprisoned not more than five years, or both.